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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Synthetic Resin Compositions and methods for the Coating, Printing or Decorating of Glass therewith

We, AUSTRALIAN CONSOLIDATED INDUSTRIES LIMITED, of 500 Bourke Street, Melbourne, in the State of Victoria, Commonwealth of Australia, being a company incorporated under the laws of the State of Victoria, Commonwealth of Australia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates generally to the coating or decoration of glass surfaces and is particularly concerned with polymeric compositions and methods for applying coatings and printing and decorating directly to glass surfaces.

Synthetic resin coatings have heretofore been used for application to glass surfaces. Although such resin coatings appear to have some satisfactory physical characteristics for limited applications whereby they exhibit satisfactory gloss, hardness and flow characteristics, the known compositions generally do not have sufficient continued adhesion to glass and furthermore, exhibit low resistance to action of alkali. In the former instance initial adhesion commonly deteriorates over a few months so that the ink is readily chipped from the surface. The latter defect is most pronounced when the resin coating is subjected to alkali washing employed before use of the article.

Glass surfaces such as tumblers and bottles, are often printed by silk screening, employing an ink based on a coloured glass frit dispersed in an oil.

The process involves firstly applying the ink to the required areas of the glass followed by a preliminary drying step. The prints are then fused at temperatures up to 1200° F to burn off the oil, sinter the frit into the glass surface and anneal the glass. This firing takes several hours.

The print achieved is very durable but has some inherent disadvantages. Since the colour is applied by means of coloured glass frit, the available colours are necessarily restricted to those of coloured glass, i.e. the colours obtained as colloidal dispersions of metal, metal oxide or sulphide and metal silicates. Colouring materials which would be effected by the high temperatures encountered cannot be used. The covering power of coloured glass is low and hence high builds of ink are normally necessary to achieve the required opacity.

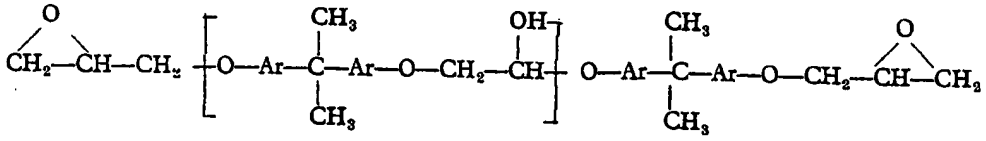
The drying and firing process is lengthy and expensive and the comparatively high quantity of fuel required represents a considerable increase in the cost of the finished article. In addition, the time taken by the process necessitates the provision of a large furnace if a satisfactory output rate is to be achieved.

The overall dimensions of the bottle manufacturing and printing equipment are such that it is normally necessary to transport the glass from the lehr to a separate factory for printing.

The additional cost of the above process as compared with the cost of paper labels can usually be justified in the case of such articles as soft drink bottles which are re-used several times before being finally discarded. However, there has recently arisen a strong demand for thin, non-returnable jars and bottles with permanently printed advertising and other matter thereon, but the cost is usually found to be prohibitive.

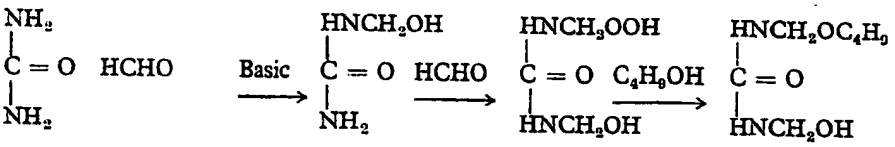
Consequently it would be of advantage to have a process which:

(a) can be carried out at comparatively low temperatures



Where Ar = e.g. Epikote (Registered Trade Mark) 1007 (epoxide equivalent 1650—2050) a product of Shell Chemicals.

(b) Any butylated urea formaldehyde resin made by reacting urea, formaldehyde and butanol by the following complex type reactions.



e.g. Butylated urea formaldehyde resin BU640 supplied by Monsanto Chemicals and has 60% non-volatile and contains solvent comprising xylol and butanol (ratio 2/1).

When it is desired not merely to apply the above coating to glass surfaces, but also to colour print or decorate the glass surface, then organic or inorganic pigments, dyes and colouring agents are added to the composition.

The pigment or dyes suitable for ink manufacture may be used in conjunction with epoxy / butylated urea formaldehyde resin within the following range:

(A) Pigment or dye	10%—30% by volume
(B) epoxy/butylated urea formaldehyde resin	90%—70% by volume

In the manufacture of printing inks suitable for printing and/or decorating the surface of glass containers using substituted organosilanes the epoxy resin in combination with butylated urea formaldehyde resin should be present within an amount ranging from:

(a) epoxy resin	80%:60%
(b) butylated urea formaldehyde resin	20%:40%

The pigments used in the ink manufacture may be of the type:

(a) White pigments such as rutile (titanium dioxide) manufactured by either chlorinated or sulphate process and having a particle size, e.g. Austiox RCR 3 supplied by I.C.I.

(b) Pigments or dyes suitable for use with epoxy resins e.g.

(i) yellow pigments or dyes such as the Benzidine type yellow pigment as supplied by Geigy as Irgalite Yellow BAF. Irgalite is a Registered Trade Mark.

(ii) Blue pigments or dyes such as the chlorinated Indanthrene Blue Pigment as supplied by Geigy as Irgalite Blue 2RS.

Although the precise amount of pigments, dyes or colouring and decorating agents is not critical for the purposes of this invention, for economical reasons the amounts should be kept to a minimum. Furthermore the type of pigment or dye is not critical and any of a number of available and economically suitable pigments or dyes can be used. Thus the coating composition may be employed with any pigments or dyes commonly employed in surface coatings.

In another aspect of the invention the organosilane is added to a mixture of epoxy resin/aminoaldehyde resin in a suitable solvent shortly before the composition is to be applied to glass. This aspect applies to the coating composition with or without colouring or decorating agents.

A further characteristic of the above composition is that it can be applied directly to glass surfaces without separate use as a primer and the invention thus provides a one-pot composition which is applied as a single coating.

Generally speaking, when the above composition is used with an ink for the printing or decoration of glass containers the amount or organosilane present is controlled within the range of 0.2% to 20% by weight of the two resin components.

TABLE 1 (cont.)

Colour of Ink	Percent by Weight		
	Formula No. 1 Yellow	Formula No. 2 Blue	Formula No. 3 White
(c) Wetting agent			
Nuosperse 657 Nuosperse is a Registered Trade Mark a product supplied by Nuodex	0.33	0.30	0.209
(d) Pigment			
1. Titanium dioxide manufactured by chlorinated or sulphate process (TiO_2) e.g. Austiox RCR_3 supplied by I.C.I.	18.20	16.71	23.60
2. Yellow pigment e.g. organic pigment Benzidine yellow supplied by Geigy as Irgalite BAF	2.82	—	—
3. Blue pigment e.g. an organic chlorinated Indanthrene Blue pigment e.g. supplied by Geigy as Irgalite 2RS	—	2.81	—
4. Gelling agent capable of thickening epoxy resins in ketones and glycol ethers e.g. Bentone 27 supplied by Abbey Chemicals, U.K. Bentone is a Registered Trade Mark	1.06	0.95	0.94
(e) Solvents			
1. Glycol ethers e. g. Carbitol Carbitol is a Registered Trade Mark ($CH_3.CH_2O.CH_2.CH_2.O.CH_2.CH_2.OH$) a product by Union Carbide	22.78	20.45	20.30
2. Ketones e.g. Diacetone alcohol	13.69	21.76	18.10
3. Methyl isobutyl ketone (M.I.B.K.)	0.77	0.69	0.69
	100.00	100.00	100.00

The invention has led to many applications to glass surfaces.

e.g. (a) Spraying of transparent and pigmented lacquers on light fittings, glass tumblers, window glass, light globes and cosmetic containers.

(b) Printing of transparent Inks on cosmetic containers and tumblers.

(c) Printing multicolours by offset lithography. For spraying opaque finishes on light fitting, opal glass and cosmetic containers the polymeric ink formulations in Table 1 are used. The spray formulations are prepared in the following manner.

Example	Parts by Volume
White Printing Ink Formulation No. 3	60.0
Spraying Thinners: Butyl Cellosolve 25%, Toluol 75%	40.0
	100.00

Cellosolve is a Registered Trade Mark of Union Carbide

The viscosity of the final pigmented finish depends on type of spray gun used.

For spraying transparent lacquers for light fittings and tumblers, dyed formulations employing different solvent balance are used. Table 3 illustrates formulations embodying the other novel features of the invention. These formulations are based on dyes with good heat stability and chemical resistance. The transparent coating is baked for 20 minutes at 400±25° F to give excellent adhesion, transparency, colour stability, light stability and detergent resistance. The actual time of bake will depend on the heat capacity of the article.

TABLE 4

	Formula	Brookfield Viscosity No. 4 20 RPM 23°C	Burrel-Seevers Rheometer 30°C
Yellow	1	100—130 poises	70—100 grams/100 sec.
Blue	2	80—100	50—80
White	3	80—100	80—100
Black	4	110—130	170—195
Red	5	75—90	125—145
Green	6	75—90	80—95

Finally, the aminopropyltriethoxysilane was added to this polymeric mixture one half hour before use to ensure suitable viscosity, stability and mixing before being printed on glass articles or surfaces. If it is intended to use the composition for printing on glass through a silk screen, then for optimum results the particle size of the ink on a Hegman grind gauge should be less than 5 microns. The resultant pigmented or coloured composition is applied onto glass articles, in this case bottles, by a silk screen, which is coated with a polyvinyl alcohol resin. Alternatively the liquid composition is sprayed at room temperature onto the exterior surfaces of 13 oz. bottles which are continuously moved past the spraying zone on a conveyor, and are preferably rotated about their vertical axis to ensure more uniform distribution of the coating.

After application of the coating, the coated bottles are then cured by heating so as to react and cure the polymeric components and chemically bond the composition to the glass surface. Curing is most suitably and economically effected by rotating the printed bottles with a low temperature gas flame so that the heating time is only from 6 to 10 seconds an interval, sufficient to react and cure the composition and chemically bond the coating to the glass, but insufficient to cause discoloration of the pigment.

It is also possible to coat the articles by dipping and to cure the composition to a hard, durable state by baking in an electric or gas oven in a temperature range of 300° F to 600° F for from 5 minutes to 20 minutes. These conditions are however, more suitable for reacting and curing compositions without dyes or pigments. The optimum heating and curing temperature for use on glass articles which have been printed or decorated is 400 ±25° F.

The following is a more detailed description of techniques used in carrying out the method of this invention:—

a) *Composition Preparation:* 10 grams aminoalkylsilane (Union Carbide (A1100) is added to 1000±10 grams pigmented epoxy butylated urea resin (in Table 1) one half hour before application to ensure suitable viscosity stability and mixing before printing.

The sample is extruded through a Burrel Severs Rheometer with an orifice 0.3318 cms. in diameter at a pressure of 30±1 p.s.i. for 15 secs.

The printing ink when mixed with aminoalkylsilane has a useful pot life of up to one week. To obtain the best printing properties diacetone alcohol is used for thinning to a suitable application viscosity of the silk screen.

b) *Printing Machine:* The polymeric ink rheological properties were designed to be used on a Solar Semi-automatic Printing Machine (Solar is a Registered Trade Mark), Pranz Brockmann Fully-Automatic Machine and A.G.M. designed manual operated Machine. The printing machine uses a free squeegee to take the variation in glass surfaces. The Solar Printing Machine operates at speeds of 40—50 bottles per minute on 13 oz. soft drink bottles, while the Pranz Brockmann Machine prints at speeds of 100—120 tube vials per minute.

c) *Silk Screen Preparation:* For best print definition of the silk screen should be made on No. 212 Nylon for printing 13 oz. soft drink bottles and up to No. 350 Nylon for printing cosmetic containers. The silk screen pattern is made up of polyvinyl alcohol supplied by Du Pont as ELVANOL. The silk screen showed no attack by any of the solvents or resins used in the polymeric ink formulations.

d) *Application:* 1000 grams of organic ink with aminoalkyl silane made up on example formulations 1—6 in Tables 1 and 2 can print 100 gross of 13 oz. non-returnable bottles. If the bottle temperature falls below 70° F the adhesion of the ink may deteriorate

The coatings were applied with a 3 thou Gradner drawn down applicator and baked for 7 mins. at 400° F. Taber Adhesion Tests were recorded in grams.

a) After ½ hour, 3 days and 3 months standing at 70±5° F.

b) After alkali washing with a 3% Solgon solution for ½ hour at 160° F and after 3 days standing at 70±5° F.

Tables 5, 6 and 7 show the Taber Adhesion results in grams for the three silanes against a control without silane.

TABER ADHESION RESULTS IN GRAMS

Batch No.	1 Percent	Standing	Standing at 70 ± 5°F			Alkali Washing with 3% Solgon	
	Silane Addition	Time with Silane	½ hour	3 Days	3 Months	—	3 days
1	None		310	290	100	270	140
2	Silane A1100	20 mins	230	300	390	340	330
3	Silane Y4086	30 mins	280	310	300	310	260
4	Silane Y4087	30 mins	240	230	290	300	360
5	Silane A1100	5 hours	x	370	345	320	360
6	Silane Y4086	5 hours	x	390	310	300	240
7	Silane Y4087	5 hours	x	400	300	310	330

The above results show that the Silane A1100 used in all our formulations 1—9 has slightly better adhesion than Silanes Y4086 and Y4087, and far greater adhesion than without silane.

TABLE 6

Room Temperature Bottles
Taber Adhesion in Grams

	Conditions	Control 2 wks.	4 wks.	10 wks.	14 wks.	17 wks.	6 mths.
A	Alkali Washed 130°F for 10 minutes	110	115	100	120	140	90
B	Alkali Washed 160°F for 10 minutes	120	95	100	100	120	110
C	Aged Bottles before washing	120	115	100	120	130	110
	Alkali Washed 130° for 10 minutes	100	105	95	80	95	90
D	Aged bottles before washing	120	110	95	130	140	120
	Alkali Washed 160°F for 10 minutes	110	110	80	90	80	100

amine-aldehyde resin and at least one organic solvent or dispersant, adding to the mixture before use an organosilane as herein defined, applying the liquid composition so formed directly to a glass surface, then heating the coated glass surface at a temperature and for a time sufficient to react and cure the components of the composition and obtain adherence thereof, to glass.

16. A method according to Claim 15, wherein the liquid composition contains from 80% to 60% by weight of the epoxy resin, from 20% to 40% by weight of the amine-aldehyde resin and from 0.2% to 20% by weight of the organosilane, all of said components being dissolved in a suitable solvent.

17. A method according to Claim 16, wherein the epoxy resin is formed by condensation of epichlorhydrin and diphenylolpropane and has a molecular weight range between 2000 to 4000.

18. A method according to Claim 16, wherein the organosilane is an aminoalkyltrialkoxysilane.

19. A method according to Claims 15 to 18, wherein the polymeric mixture additionally contains in solution or suspension at least one pigment or dye.

20. A method according to Claim 19, wherein the mixture additionally contains a gelling, antifoaming or wetting agent.

21. A method according to any of Claims 15 to 20, wherein the polymeric mixture is used as a printing ink for printing or decorating glass articles by applying directly to the glass surface the liquid composition using a silk screen.

22. A method of using the composition of Claim 11, wherein the liquid composition is applied to glass surfaces by spraying at ambient temperatures.

23. A method according to Claim 22, wherein the organosilane of the type specified as γ-aminopropyltriethoxysilane is added to the polymeric mixture approximately 30 minutes before the composition is applied to glass.

24. A method according to Claim 22, wherein the glass surface coated with the liquid composition, is heated at a temperature between 300° F and 600° F.

25. A method according to Claim 23, wherein the coated glass surface is heated for 5 minutes to 20 minutes.

26. A method according to any one of Claims 15 to 24, wherein the composition is reacted and cured by rapidly heating the coated glass surface or article and the coated glass surface or article is then cooled to ambient temperature.

27. A method according to Claim 26, wherein the coated glass surface or article is heated by a low temperature flame for 6 to 10 seconds and is cooled to ambient temperatures in 20 to 30 seconds.

28. A method of coating or colouring glass articles comprising spraying the composition of any one of Claims 1 to 18 directly onto the exterior surfaces of the glass articles while continuously rotating and moving the articles on a conveyor, rapidly heating the coated surfaces of the articles to react and cure the components of the composition and then cooling the articles to ambient temperatures.

29. A method according to Claim 25, wherein the coating is applied to the glass surfaces as a single composition without separate application of primer coating to the glass surface.

30. A method of coating glass articles or surfaces as claimed in Claim 15 and substantially as herein described.

31. Glass articles or surfaces coated with the composition according to Claim 1 substantially as herein described.

32. Glass articles or surfaces printed or decorated with a composition comprising the reaction product of an epoxy resin an amine-aldehyde resin and an organosilane as herein defined, and including at least one pigment or dye.

33. A composition as claimed in Claim 1 and substantially as herein described.

34. A coating prepared by the method of Claim 15 and substantially as herein described.

35. An ink composition as claimed in Claim 11 and substantially as herein described.

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